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NANO-Fe_3O_4@ZrO_2 SUPPORTED PHOSPHOMOLYBDIC ACID-CATALYZED SYNTHESIS OF 3-AMINOALKYLATED INDOLES

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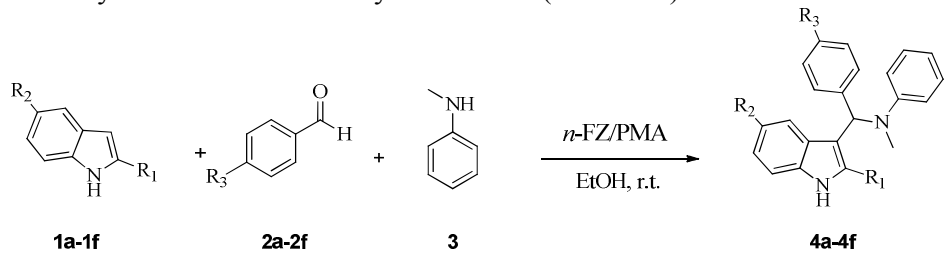
ABSTRACT
Nano-Fe_3O_4@ZrO_2supported phosphomolybdic acid (nano-Fe_3O_4@ZrO_2/PMA)-catalyzed three-component coupling reaction between indoles, aldehydes, and *N*-methyl anilineisreported to access substituted 3-aminoalkylated indoles in ethanol at room temperature in high yields (89–96%) within 14–25 min. The salient features of this protocol are the simplicity of the procedure, the ready accessibility of the catalyst, its cost effectiveness, easy recoverable by a permanent magnet, and higheryields in relatively short reaction times.

KEYWORDS: Nano-Fe_3O_4@ZrO_2supported phosphomolybdic acid; *N*-methyl aniline; 3-aminoalkylated indoles, Reusability; Short reaction time.

INTRODUCTION
3-Substituted indole moieties are ofmuchimportance as they arewidely distributed in nature and reveal a broad range of biologicalactivities[i].Indoles with aminoalkyl/aryl substituents at the 3-positionare considered as venerable pharmacophoresin drug discoveryand are found in various natural products[ii] such as 5-HT1B/1D withreceptor agonist activities used in the treatment of migraine, aromataseinhibitor for breast cancerand HIV-1 integrase inhibitors[iii]Gramine, Ergine, and Sumatriptant. The immense potential of indolenucleus as drug candidates prompted among the synthetic chemiststo explore different methods suitable for the synthesis of 3-substitutedindoles.
Many synthetic protocols were developed to accelerate the rate of 3-aminoalkylated indoles reaction and to improve the yield. These compounds have been synthesized in the presence of various catalysts such as$PMA–SiO_2$[iv], 3-Chlorophenylbornic acid (CPBA)[v], bromodimethylsulfonium bromide (BDMS)[vi],Silver triflate(AgOTf)[vii], $Yb(OTf)_3/SiO_2$[viii], PANI-HBF4[ix], $Fe(HSO_4)_3$[x], $ZrOCl_2·8H_2O$[xi], $CuCl_2·2H_2O$[xi].Major drawbacks of these procedures include expensive reagents, use of large amounts of organic solvents, prolonged heating and side reactions.
As a part of our program aiming at developing heterogeneous catalysts and modification of different support materials[xii-xxiii]we studied application of core-shell zirconia-coated magnetic

nanoparticles supported phosphomolybdic acid (nano-Fe_3O_4@ZrO_2/PMA)as an efficient acid catalyst in the synthesis of 3-aminoalkylated indoles **4** by the reaction ofindoles**1**, aldehydes**2**, and *N*-methyl aniline**3**. Nano-Fe_3O_4@ZrO_2/PMA (*n*-FZ/PMA) could be readily separated from the reaction mixture by a permanent magnet and reused several times. The process is more effective than filtration and centrifugation in preventing loss of the solid catalyst. However, there were no reports on application of *n*-FZ/PMA as an acidic heterogeneous catalyst in the synthesis of 3-aminoalkylated indoles(Scheme 1).



1a-1f **2a-2f** **3** **4a-4f**

Scheme 1. Synthesis of 3-aminoalkylated indoles catalyzed by *n*-FZ/PMA.

EXPERIMENTAL

All chemicals were purchased from Fluka (Buchs, Switzerland) or Merck Companies and used without further purification. FT–IR spectra were recorded for KBr disks on a Tensor 27 Bruker Spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a BRUKER DRX-300 AVANCE spectrometer in $CDCl_3$as solvent.

General experimental procedure

To a magnetically stirred solutionof indoles(1 mmol), aldehydes(1 mmol),*N*-methyl aniline(1mmol), and *n*-FZ/PMA (0.08 g), 5 mml of ethanol was added and stirred for appropriate time. The reaction was monitored by TLC. Upon completion of the transformation the catalyst was filtered under hot conditions. The catalyst was separated using an external magnet and washed with hot ethanol (10 mL).After cooling, the combined filtrate was allowed to stand at room temperature. The precipitated solid was collected by filtration, and recrystallized from ethanol to give desired compounds in high yields.

***N*-((1H-indol-3-yl)(phenyl)methyl)-*N*-methylaniline (4a):** FT-IR (KBr, cm^{-1}): 444, 589, 742, 1448,1623, 2865, 2982, 3403, 3379; ^{1}H NMR(300 MHz, $CDCl_3$): δ 2.69 (s, 3H, CH_3), 5.52 (s, 1H, CH), 6.57 (d, *J* = 8.1 Hz, 3Haromatic H), 6.10–7.05(m, 3H, aromatic H), 7.10–7.35 (m, 9H, aromatic H), 7.81(br. s, 1H, NH);^{13}C NMR (75 MHz, $CDCl_3$): δ31.21,48.12, 111.02, 112.41, 119.23, 120.59, 122.01, 124.11,125.92, 126.95, 127.99,128.52, 129.69, 133.19, 136.42, 144.78, 147.32; Anal.Calcd. for$C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.43; H, 6.39; N, 8.92.

***N*-((5-methoxy-1H-indol-3-yl)(4-methoxyphenyl)methyl)-*N*-methylaniline (4b):**FT-IR (KBr, cm^{-1}): 421, 565, 729, 1452,1641, 2896, 2939, 3403;^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H, CH_3), 3.21 (s, 3H, CH_3),3.43 (s, 3H, CH_3),5.58 (s, 1H, CH),6.39 (d, *J* = 8.2 Hz, 1H, aromatic H),6.50–6.56 (m,1H, aromatic H),6.65–6.70 (m, 3H, aromatic H),6.77 (s, 1H, aromatic H),6.80 (d, *J* = 8.2 Hz, 2H, aromatic H),6.88 (d, *J* = 8.2 Hz, 1H, aromatic H),7.10 (d, *J*= 4.3 Hz, 1H, aromatic H),7.20-7.25 (m, 3H, aromatic H),8.01 (br. s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.65, 46.63, 55.22, 55.44, 102.21, 110.93, 111.52, 112.62, 113.32, 118.85, 125.11, 128.01, 128.92, 128.31, 130.09, 132.25, 137.28, 154.65, 157.28;Anal.Calcd. for$C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found: C, 77.33; H, 6.42; N, 7.48.

***N*-((5-methoxy-1H-indol-3-yl)(phenyl)methyl)-*N*-methylaniline(4c).**FT-IR (KBr, cm^{-1}): 480, 812,1175, 1211, 1492, 1579, 1613, 2934,3059, 3475;^{1}H NMR (300 MHz, $CDCl_3$): δ 2.79 (s, 3H, CH_3),3.78 (s, 3H, CH_3), 5.55 (s, 1H, CH), 6.47(d,*J* = 6.9 Hz, 2H, aromatic H), 6.77 (t,*J* = 7.2 Hz, 2H, aromatic H), 6.90–7.00 (m, 3H, aromatic H),7.10–7.15 (m, 3H,

aromatic H), 7.18–7.30 (m, 2H, aromatic H), 7.35 (d,*J* = 7.1 Hz,2H, aromatic H), 7.89(br. s, 1H, NH);^{13}C NMR (75 MHz, $CDCl_3$): δ29.28, 46.92, 55.25, 111.42, 112.32, 113.45, 117.54,118.89,119.25, 120.04, 120.22, 121.77, 122.42, 123.41, 123.92, 124.58, 129.60, 129.96, 133.33, 135.25, 136.22,136.99;Anal. Calcd. for $C_{23}H_{22}N_2O$: C, 80.67; H,6.48; N, 8.18. Found: C, 80.58; H, 6.69; N, 7.80.

***N*-((4-chlorophenyl)(2-methyl-1H-indol-3-yl)methyl)-*N*-methylaniline (4d)**. FT-IR (KBr, cm^{-1}): 475, 823,1122, 1228, 1482, 1524, 1621, 2985,3100, 3425;^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.12 (s, 3H, CH_3), 2.92 (s,3H, CH_3), 5.82 (s, 1H, CH), 6.59 (d, *J*= 8.2 Hz, 1H, aromatic H), 6.77–6.86 (m, 2H, aromatic H), 6.92 (t, *J* = 8.2 Hz, 1H, aromatic H), 6.94–7.07 (m,3H, aromatic H), 7.11 (d, *J* =8.2 Hz, 1H, aromatic H), 7.14–7.20 (m, 5H, aromatic H),7.78 (br. s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$):δ29.51,38.68, 46.45, 110.05, 110.21, 112.72, 113.89, 114.95, 119.22,119.85, 120.72, 120.91, 128.29, 128.81, 129.92, 130.45, 131.62,131.88, 135.11, 135.25, 142.38, 143.69, 145.71; Anal. Calcd.for$C_{23}H_{21}N_2Cl$: C, 76.55; H, 5.87; N, 7.76.Found: C, 76.61, H, 5.79, N, 7.75.

***N*-((4-bromophenyl)(1H-indol-3-yl)methyl)-*N*-methylaniline(4e).**FT-IR (KBr, cm^{-1}): 452, 532, 771, 1103, 1459, 1524, 1613, 2985, 3022, 3125, 3452; ^{1}H NMR (300MHz, $CDCl_3$): δ2.79 (s, 3H, CH_3), 5.5 (s, 1H), 6.58–6.60 (m, 3H, aromatic H), 7.00 (d,*J* = 6.3 Hz, 2H, aromatic H), 7.15–7.20 (m, 4H, aromatic H), 7.22–7.26 (m, 3H, aromatic H), 7.36 (s, 1H, aromatic H), 8.21 (br. s, 1H, NH);^{13}C NMR (75 MHz, $CDCl_3$):δ 28.89, 46.58, 111.02, 112.23, 118.96, 119.52, 121.84, 123.56, 123.81, 124.92, 126.76, 129.74, 131.85, 133.83, 135.90, 147.77, 149.52, 153.65;Anal. Calcd.for$C_{22}H_{19}N_2Br$: C, 67.53; H, 4.89; N, 7.16.Found: C,67.49, H,4.82, N, 7.09.

***N*-((5-bromo-1H-indol-3-yl)(phenyl)methyl)-*N*-methylaniline(4f).**FT-IR (KBr, cm^{-1}): 469, 529, 763, 1100, 1453, 1521, 1642, 2998, 3058, 3101, 3398; ^{1}H NMR (300MHz, $CDCl_3$): δ 2.63 (s, 3H, CH_3), 5.56 (s, 1H, CH), 6.55–6.60 (q,*J* = 7.9 Hz, 3H, aromatic H), 6.98 (d,*J* = 7.2 Hz, 2H, aromatic H), 7.15–7.20 (m, 4H, aromatic H), 7.25–7.30 (q, *J* = 7.9 Hz, 3H, aromatic H), 7.35 (s, 1H, aromatic H), 8.09 (br. s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$):δ 28.97, 47.52, 111.23, 112.39, 119.52, 119.66, 122.27, 123.54, 123.98, 124.33, 126.78, 129.63, 130.92, 133.54, 136.58, 148.22, 149.68, 153.79; Anal. Calcd.for$C_{22}H_{19}N_2Br$: C, 67.53; H, 4.89; N, 7.16.Found: C,67.50, H, 4.82, N, 7.11.

***N*-methyl-*N*-((2-methyl-1H-indol-3-yl)(p-tolyl)methyl)aniline (4g).** FT-IR (KBr, cm^{-1}): 449, 671, 796, 856, 1429, 1588, 1611, 2932, 3079, 3401; ^{1}HNMR (300 MHz, $CDCl_3$):δ1.89 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.87 (s, 3H, CH_3), 5.89 (s, 1H, CH), 6.58 (d, *J*= 8.2 Hz,1H, aromatic H), 6.70–6.80 (m, 2H, aromatic H), 6.90–7.00 (m, 8H, aromatic H), 7.08 (d, *J* = 8.1 Hz, 1H, aromatic H), 7.10–7.15 (m, 1H, aromatic H), 7.54 (br. s, 1H, NH);^{13}C NMR (75 MHz, $CDCl_3$):δ30.01, 31.41, 38.75, 46.62, 110.02, 111.21, 112.08, 113.61, 117.41, 119.24, 119.85, 120.21,120.65, 128.52, 128.91, 129.12, 129.91, 132.58, 135.12, 135.84, 136.20, 140.21, 141.45, 146.41;Anal. Calcd.for$C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23.Found: C,84.61, H, 7.08, N,8.20.

***N*-[(4-Chlorophenyl)(5-methoxy-1H-indol-3-yl)methyl]-*N*-methyl benzenamine (4h):**FT-IR (KBr, cm^{-1}): 451, 669, 802, 878, 1425, 1580, 1625, 2973, 3082, 3421; ^{1}H NMR (300 MHz, $CDCl_3$): δ2.82 (s, 3H, CH_3), 3.68 (s, 3H, CH_3),5.93 (s, 1H, CH),6.50–6.95 (m, 6H, aromatic H),7.11 (d, *J* = 6.8 Hz, 2H, aromatic H),7.20–7.30 (m, 4H, aromatic H),7.82 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ23.59, 33.94,45.75, 60.09, 105.89, 113.23, 115.52, 119.39, 125.62, 126.25, 127.22, 128.75,129.96, 131.86, 135.66, 143.78, 149.52, 157.21;Anal. Calcd.for$C_{23}H_{21}N_2O$: C, 73.30; H, 5.62; N, 7.43.Found: C,73.27, H, 5.58, N,7.39.

RESULT AND DISCUSSION

Characterization of the catalyst

The nano-Fe_3O_4@ZrO_2/PMAcatalyst was prepared according to the literature procedure[xxiv].The *n*-FZ/PMA was characterized by FT-IR, andX-ray diffraction (XRD).

The FT-IR spectrums of nano-ZrO_2, nano-Fe_3O_4,nano-Fe_3O_4@ZrO_2, PMA and also nano-Fe_3O_4@ZrO_2/PMA are shown in Figure 1, curves a-e, respectively.In Figure 1(a), the characteristic vibrational bands of the Zr–O bond at 578 and 755 cm^{-1}, as well band belonging to the Zr–OH group at 1627 cm^{-1}[xxv]. The characteristic absorption band of Fe_3O_4 appears at 593 cm^{-1} in Figure 1(b). The spectrum of the Fe_3O_4@ZrO_2 nanoparticles (Figure 1(c)) shows a new absorption peak related to the characteristic absorption of zirconia at 624 cm^{-1} which confirmed the successful formation of Fe_3O_4@ZrO_2nanoparticles[xxvi]. The FT-IR spectrum of Fe_3O_4@ZrO_2/PMA nanoparticles (Figure 1, curve e) showed new peaks at 1081, and 972 cm^{-1} related to the P-O and Mo=O_{tet} stretchingvibrations, respectively, and also two absorption at 839 and 778 cm^{-1} attributed to the Mo-O_c-Mo and Mo-O_e-Mo stretching vibrations, respectively. According to the PMA absorptions (Figure 1, curve d) it can be concluded that PMA has been supported on Fe_3O_4@ZrO_2[xxvii]. The absorbance appeared at 1648 and 3321 cm^{-1} are attributed to the presence of –OH and H–O–H groups.

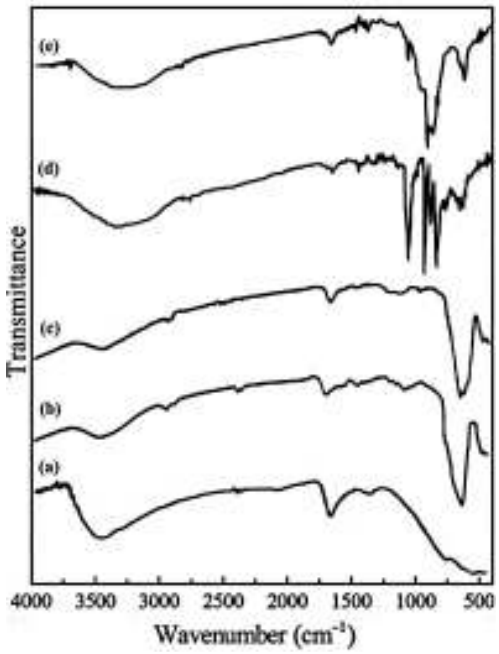


Figure 1. FT-IR spectra of (a) nano-ZrO_2, (b) nano-Fe_3O_4, (c) nano-Fe_3O_4@ZrO_2, (d)PMA, (e) nano-Fe_3O_4@ZrO_2/PMA.

The XRD patterns of the prepared nano-Fe_3O_4, nano-Fe_3O_4@ZrO_2, and nano-Fe_3O_4@ZrO_2/PMA are presented in Figure 2. In Figure 2(a), the signals at the values of 2θ equal to 30.23 (220), 35.10 (311), 43.26 (400), 53.51 (422), 56.06 (511) and 63.11 (440) corresponds to cubic structure of $Fe_3O_4$and has good agreement with (JCPDS file PDF no. 65-3107)[xxviii]. The XRD pattern of the nano-Fe_3O_4@ZrO_2 sample (Figure 2(b)) shows peaks at 31.02˚ and 36.23˚ belong to Fe_3O_4 which have shifted from 30.23˚ and 35.10˚, respectively. Besides the peaks for Fe_3O_4, two small nonmagnetic related peaks located in 50.21˚ and 60.52˚ are found which can be indexed to the diffraction of (112) and (211) planes of the standard data for ZrO_2 (JCPDS file no. 88-1007)[xxix].In thediffractogram of nano-

Fe_3O_4@ZrO_2/PMA no characteristic peaks of PMA can be detected. Thisindicates that heteropolyacid species are well-dispersed on the surface of nano-Fe_3O_4@$ZrO_2$and there is not any crystalline phase of polyoxometalates in the resultednanomaterials (Figure 2(c))[xxx-xxxi].

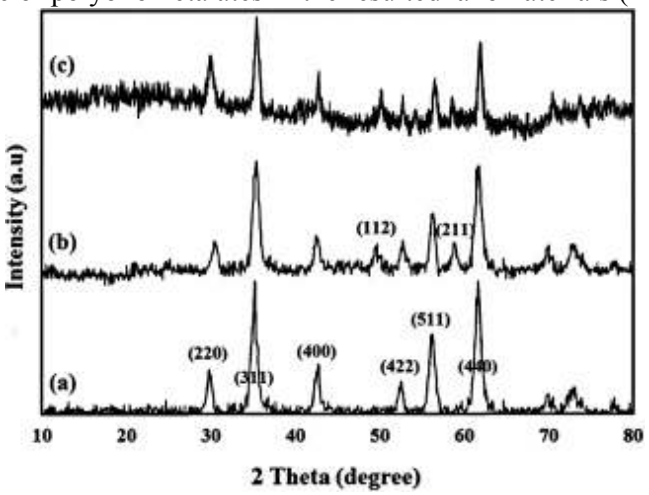


Figure 2. XRD patterns of(a) nano-Fe_3O_4, (b) nano-Fe_3O_4@ZrO_2,(c)nano-Fe_3O_4@ZrO_2/PMA.

Evaluation of catalytic activity of n-FZ/PMA in the synthesis of 3-aminoalkylated indoles.
For the beginning of this study, benzaldehyde**2a** was employed as the model aldehyde reacted with *N*-methyl aniline **3** and indole**1a**. In order to get the effective reaction conditions, the reaction was optimized in terms of various parameters like catalyst amount, effect of solvent, and influence of temperature (Table 1). Low yields of the product **4a** were obtained in the absence of the catalyst at room temperature (entries 1-3) or in the presence of the catalyst under solvent-free conditions at high temperatures (entries 4 and 5) indicating that the catalyst and solvent are necessary for the reaction. As can be seen from Table 1, among the tested solvents such as H_2O, EtOH, MeOH, $CHCl_3$, CH_3CN, and also solvent-free conditions and various amounts of the catalyst, the reaction was more facile and proceeded to give the highest yield, using 0.08 g of *n*-FZ/PMA in EtOH at room temperature (entry 11). All subsequent reactions were carried out in these optimized conditions.

Table 1. Optimization of reaction conditions for the synthesis of compound **4a**catalyzed by *n*-FZ/PMA.*

Entry	Catalyst (g)	Solvent	T/°C	Time/min	Isolated Yield/%
1	----	----	r.t.	100	26
2	----	H_2O	r.t.	100	35
3	----	EtOH	r.t.	100	39
4	0.08	----	100	40	77
5	0.08	----	120	40	79
6	0.06	H_2O	r.t.	36	75
7	0.08	H_2O	r.t.	30	79
8	0.02	EtOH	r.t.	40	56
9	0.04	EtOH	r.t.	35	78
10	0.06	EtOH	r.t.	25	89
11	**0.08**	**EtOH**	r.t.	**15**	**95**
12	0.08	EtOH	50	15	89
13	0.08	EtOH	Reflux	15	93
14	0.1	EtOH	r.t.	15	94

15	0.06	MeOH	r.t.	20	82
16	0.08	MeOH	r.t.	15	85
17	0.08	$CHCl_3$	r.t.	20	89
18	0.08	CH_3CN	r.t.	20	80

[*] Reaction conditions: Indole**1** (1 mmol), benzaldehyde**2a**(1 mmol), and *N*-methyl aniline**3**(1 mmol).

According to these results, and to generalize this model reaction, we developed the reaction of *N*-methyl aniline**3**with the different kinds of indoles **1** and various aryl aldehydes **2** under the optimized reaction conditions (Table 2). The *n*-FZ/PMA efficiently catalyzed the reactions, giving the desired products in high yields over relatively short reaction times. Easy separation of obtained products from the catalyst makes this method useful for the synthesis of 3-aminoalkylated indoles.

Table 2. Synthesis of different3-aminoalkylated indoles[a].

Entry	R_1	R_2	R_3	Product	Time (min)	Yield (%)	M.p. (°C)	
							Found	Reported
1	H	H	H	**4a**	15	96	142-144	145-147[iv]
2	H	OMe	OMe	**4b**	14	93	205-207	207-209[vii]
3	H	OMe	H	**4c**	15	94	185-187	186-190[ix]
4	Me	H	Cl	**4d**	21	90	205-207	208-210[vii]
5	H	H	Br	**4e**	16	91	128-130	126-130[ix]
6	H	Br	H	**4f**	19	89	206-208	210-212[v]
7	Me	H	Me	**4g**	25	92	200-202	202-204[vii]
8	H	OMe	Cl	**4h**	23	89	203-205	204-206[v]

[a]Reactionconditions: Indoles **1** (1 mmol), aromatic aldehydes **2** (1 mmol), *N*-methyl aniline**3**(1 mmol), and*n*-FZ/PMA (0.08 g) in ethanol (5 ml) at room temperature.

We compared the results we obtained using *n*-FZ/PMA as catalyst with previously reported results for the synthesis of 3-aminoalkylated indolesin the presence of various catalysts (Table 3). Our reaction conditions showed shorter reaction times than all the other conditions and gave high yields of the desired products.

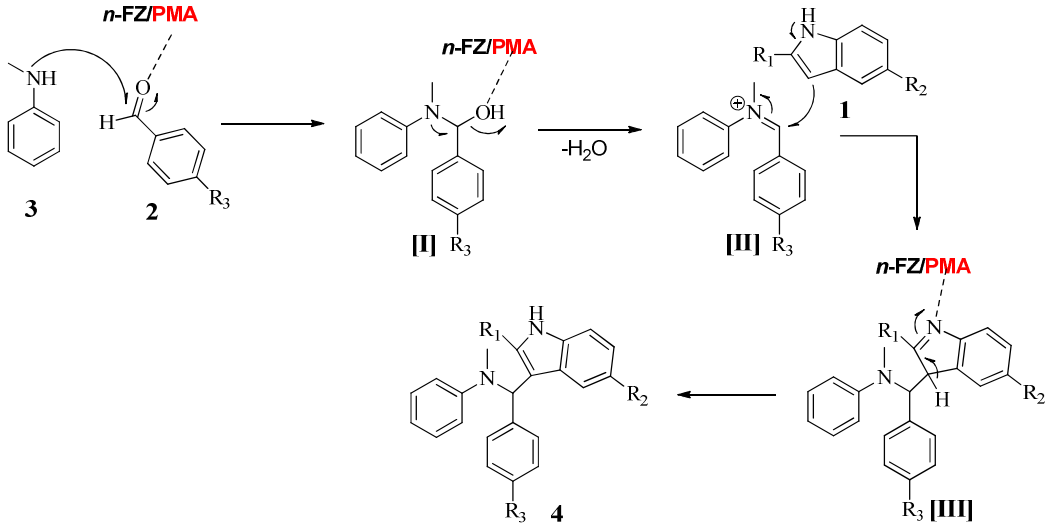
Table 3. Comparison of the efficiencies of different catalysts for the synthesis of 3-aminoalkylated indoles.

Catalyst	Conditions		Time (min)	Yield (%)	Ref.
	Solvent	T/°C			
$PMA–SiO_2$	-----	r.t.	180-240	65-85	iv
CPBA	CH_3CN	r.t.	720-840	82-90	v
BDMS	EtOH	r.t.	90-210	82-96	vi
AgOTf	CH_3CN	r.t.	240	45-86	vii
$Yb(OTf)_3/SiO_2$	CH_3CN	r.t.	120	51-88	viii
$PANI-HBF_4$	-----	r.t.	30-50	88-97	ix
$Fe(HSO_4)_3$	-----	r.t.	60-240	87-98	x
$ZrOCl_2·8H_2O$	-----	r.t.	24-150	65-96	xi
$CuCl_2·2H_2O$	-----	r.t.	30-120	64-92	xi
n-FZ/PMA	EtOH	r.t.	14-25	89-96	This work

The model reaction under optimized reaction conditions was used for evaluating reusability of *n*-FZ/PMA catalyst. Upon completion of the reaction, the catalyst was recovered as described in the experimental section. The catalyst could be used at least four times without significant reduction in its activity (96, 94, 92, 90%).

A plausible mechanism is proposed in Scheme 2. We assume that when *N*-methylaniline**3** is reacted with aromatic aldehyde **2** in the presence of *n*-FZ/PMA, an iminium ion intermediate

II is formed. An imminium ion is then attacked by an electron rich indole **1** to get the desired 3-aminoalkylated indole **4**.



Scheme 2. Plausible mechanism for the *n*-FZ/PMA catalyzed formation of 3-aminoalkylated indoles.

CONCLUSION

In this paper we developed the synthesis of 3-aminoalkylated indole derivatives in the presence of *n*-FZ/PMA as a highly effective heterogeneous catalyst. This method provided these products in high yields over short reaction time. Also, easy magnetic separation makes this catalyst attractive in view of green chemistry and catalysis science.

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